

U.S. DEPARTMENT OF COMMERCE PATENT & TRADEMARK OFFICE

B/O Form PTO-1390		Transmittal Letter to the United States Designated/Elected Office (DO/EO/US) Concerning a Filing Under 35 USC 371		Attorney's Docket Number GIER3001/JEK	
				U.S. Application Number (if known) 097926579	
International Application Number PCT/EP00/04694		International Filing Date 23 May 2000		Priority Date Claimed 25 May 1999	
Title of Invention VALUABLE DOCUMENT					
Applicant(s) for DO/EO/US Thomas GIERING et al.			Assignee		

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items under 35 USC 371:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 USC 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 USC 371.
3. ☒ This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 USC 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed 35 USC 371(c)(2).
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 USC 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 USC 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 USC 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 USC 371(c)(4)). (☒ Executed ☐ Unexecuted)
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 USC 371(c)(5)).

Items 11 to 16 below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: 3 sheets of formal drawings

Application Number (if Known) 09/926579		International Application Number PCT/EP00/04694		Attorney's Docket Number GIER3001/JEK	
				Calculations	PTO USE ONLY
17. The following fees are submitted: Basic National Fee (37 CFR 1.492(a)(1)-(5)): <input checked="" type="checkbox"/> Search report has been prepared by the EPO or JPO \$890.00 <input type="checkbox"/> International Preliminary Examination Fee paid to USPTO (37 CFR 1.482) \$710.00 <input type="checkbox"/> No International Preliminary Examination Fee paid to USPTO (37 CFR 1.482) but International Search Fee paid to USPTO (37 CFR 1.445(a)(2)) \$740.00 <input type="checkbox"/> Neither International Preliminary Examination Fee (37 CFR 1.482) nor International Search Fee (37 CFR 1.445(a)(2)) paid to USPTO \$1040.00 <input type="checkbox"/> International Preliminary Examination Fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT				\$ 890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).					
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	20 -20 =		× \$18.00		
Independent Claims	5 -3 =	2	× \$84.00	\$ 168.00	
Multiple Dependent Claims (if applicable)			+ \$280.00		
TOTAL OF ABOVE CALCULATIONS				\$ 1,058.00	
Reduction by 1/2 for filing by small entity, if applicable. Small Entity Status is asserted pursuant to 37 CFR 1.27 for this application.					
SUBTOTAL				\$ 1,058.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).					
TOTAL NATIONAL FEE				\$ 1,058.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property.					
TOTAL FEES ENCLOSED				\$ 1,058.00	
				Amount to be:	Refunded:
				Charged:	

- a. ☒ A check in the amount of \$1,058.00 to cover the fees is enclosed.
 b. ☐ Please charge my Deposit Account Number 02-0200 in the amount of \$_____ to cover the above fees.
 A duplicate copy of this sheet is enclosed.
 c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account Number 02-0200. A duplicate copy of this sheet is enclosed.

Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.



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DATE: 21 November 2001

Respectfully submitted,

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09/926579

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

International Patent Application
No. PCT/EP00/04694

PCT/DO/EO/US

International Filing Date: 23 May 2000

Attorney Docket: GIER3001/JEK

Applicant: Thomas GIERING et al.

For: VALUABLE DOCUMENT

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

This paper accompanies documents submitted to establish the U.S. national stage of the above-identified international patent application.

The claims were not amended during the international phase. Before calculation of the filing fee and before examination, please amend the application as follows:

IN THE CLAIMS:

Please amend the original as-filed claims as shown on the appended APPENDIX OF CLAIMS, which includes amended and non-amended claims. Also appended hereto an APPENDIX OF MARKED UP CLAIMS showing the changes which have been made.

REMARKS

All rights are reserved to the original claimed subject matter. The claims have been amended to reduce the filing fees and to restate the inventive subject matter in clear terms. None of the amendments are intended to narrow any element of the claims as they stood prior to amendment. Examination of the application as amended is respectfully requested.

Respectfully submitted,
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Date: November 20, 2001

09/926579-02660



23364

PATENT TRADEMARK OFFICE

International Application No. PCT/EP00/04694
Attorney Docket No. GIER3001/JEK

APPENDIX OF MARKED UP VERSION OF CLAIMS

1(Amended). A document of value [(1), such as] for example a paper of value, ID card or the like, [having] comprising at least one authenticity feature [(3)] in the form of a luminescent substance, the luminescent substance [(3)] having particles [consisting of] comprising a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission, the dye being incorporated in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve and wherein the transition to stimulated emission [being] is accompanied by a detectable change in the luminescent properties of the dye.

2(Amended). [A] The document of value [(1)] according to claim 1, [characterized in that] wherein the luminescent substance [(3) has] comprises different particles [consisting of] comprising different dye-laden molecular sieves.

3(Amended). [A] The document of value [(1)] according to claim [1 or] 2, [characterized in that] wherein the molecular [sieves with] sieve includes a channel structure, [e.g.] such as [from the] classes of aluminophosphates[, are used].

4(Amended). [A] The document of value [(1)] according to [at least one of] claims 1 to 3, characterized in that] claim 1, wherein the dye molecules [from the] comprise a class of laser dyes [are used].

5(Amended). [A] The document of value [(1)] according to [at least one of] claims 1 to 4; characterized in that] claim 1, wherein the spectral properties of the dye [are] have been adjusted by selection of the end groups.

6(Amended). [A] The document of value [(1)] according to [at least one of claims 1 to 5, characterized in that] claim 1, wherein the molecular sieve [has] includes different excitable dyes.

7(Amended). [A] The document of value [(1)] according to [at least one of claims 1 to 6, characterized in that] claim 1, wherein the document of value [(1)] has a further authenticity feature.

8(Amended). [A] The document of value [(1)] according to claim 7, [characterized in that] wherein the second authenticity feature [is] comprises a further luminescent material which preferably has the same body color as the luminescent substance.

9(Amended). [A] The document of value [(1)] according to [at least one of claims 1 to 8, characterized in that] claim 1, wherein the luminescent substance [(3)] is present in the volume of the document of value [(1)].

10(Amended). [A] The document of value [(1)] according to [at least one of claims 1 to 8, characterized in that] claim 1, wherein the luminescent substance [(3)] is admixed to a printing ink.

11(Amended). [A] The document of value [(1)] according to claim 10, [characterized in that] wherein the printing ink is applied in the form of a coding, [in particular] for example a bar code.

12(Amended). [A] The document of value [(1)] according to claim 10 [or 11], [characterized in that] wherein the printing ink with the luminescent substance is surrounded by a second printing ink with a further luminescent substance.

13(Amended). [A] The document of value [(1)] according to [at least one of claims 10 to 12, characterized in that] claim 10, wherein the printing ink is applied at least in certain areas to the document of value [(1)] or to a carrier connected with the document of value [(1)].

14(Amended). [A] The document of value [(1)] according to [at least; one of claims 1 to 8, characterized in that] claim 1, wherein the luminescent substance [(3)] is disposed in or on a security element [(2)] connected with the document of value.

15(Amended). A security element [(2) having] comprising at least one authenticity feature [(3)] in the form of a luminescent substance, the luminescent substance [(3)] having particles [consisting of] comprising a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission, the dye being incorporated in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve, and wherein the transition to stimulated emission [being] is accompanied by a detectable change in the luminescent properties of the dye.

16(Amended). [A] The security element [(2)] according to claim 15, [characterized in that] wherein the security element [(2) has] includes at least one carrier material in the volume or on the surface of which the luminescent substance [(3)] is disposed.

17(Amended). [A] The security element [(2)] according to claim 15 [or 16], [characterized in that] wherein the security element [(2)] has the form selected from the group consisting of a strip, band [or] and a label.

18(Amended). A method for marking a product comprising:

[products whereby the product is provided] providing a product with a luminescent substance having particles [consisting of] comprising a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission[.];

incorporating the dye [being incorporated] in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve, and

selecting the dye such that the transition to stimulated emission [being] is accompanied by a detectable change in the luminescent properties of the dye.

19(Amended). A method for checking a luminescent substance having particles [consisting of] comprising a dye-laden molecular sieve whose structure forms an optical resonator, comprising the steps:

[in which] selecting at least one dye that can be excited to show stimulated emission[.];

incorporating the dye [being incorporated] in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve[, and];

selecting the dye such that the transition to stimulated emission [being] is accompanied by a detectable change in the luminescent properties of the dye[.];
and

using the line narrowing and line shift and/or the threshold behavior and/or the shortening of the lifetime [being used] as an authenticity feature.

International Application No. PCT/EP00/04694
Attorney Docket No. GIER3001/JEK

20(Amended). [Use of] A process for marking products comprising using dye-
laden molecular sieves showing stimulated luminescence without an external
resonator for marking the products.

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PATENT TRADEMARK OFFICE

International Application No. PCT/EP00/04694
Attorney Docket No. GIER3001/JEK

APPENDIX OF CLAIMS

1(Amended). A document of value for example a paper of value, ID card or the like, comprising at least one authenticity feature in the form of a luminescent substance, the luminescent substance having particles comprising a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission, the dye being incorporated in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve and wherein the transition to stimulated emission is accompanied by a detectable change in the luminescent properties of the dye.

2(Amended). The document of value according to claim 1, wherein the luminescent substance comprises different particles comprising different dye-laden molecular sieves.

3(Amended). The document of value according to claim 2, wherein the molecular sieve includes a channel structure, such as classes of aluminophosphates.

4(Amended). The document of value according to claim 1, wherein the dye molecules comprise a class of laser dyes.

5(Amended). The document of value according to claim 1, wherein the spectral properties of the dye have been adjusted by selection of the end groups.

6(Amended). The document of value according to claim 1, wherein the molecular sieve includes different excitable dyes.

7(Amended). The document of value according to claim 1, wherein the document of value has a further authenticity feature.

8(Amended). The document of value according to claim 7, wherein the second authenticity feature comprises a further luminescent material which preferably has the same body color as the luminescent substance.

9(Amended). The document of value according to claim 1, wherein the luminescent substance is present in the volume of the document of value.

10(Amended). The document of value according to claim 1, wherein the luminescent substance is admixed to a printing ink.

11(Amended). The document of value according to claim 10, wherein the printing ink is applied in the form of a coding, for example a bar code.

12(Amended). The document of value according to claim 10, wherein the printing ink with the luminescent substance is surrounded by a second printing ink with a further luminescent substance.

13(Amended). The document of value according to claim 10, wherein the printing ink is applied at least in certain areas to the document of value or to a carrier connected with the document of value.

14(Amended). The document of value according to claim 1, wherein the luminescent substance is disposed in or on a security element connected with the document of value.

15(Amended). A security element comprising at least one authenticity feature in the form of a luminescent substance, the luminescent substance having particles comprising a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission, the dye being

incorporated in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve, and wherein the transition to stimulated emission is accompanied by a detectable change in the luminescent properties of the dye.

16(Amended). The security element according to claim 15, wherein the security element includes at least one carrier material in the volume or on the surface of which the luminescent substance is disposed.

17(Amended). The security element according to claim 15, wherein the security element has the form selected from the group consisting of a strip, band and a label.

18(Amended). A method for marking a product comprising:

providing a product with a luminescent substance having particles comprising a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission;

incorporating the dye in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve, and

selecting the dye such that the transition to stimulated emission is accompanied by a detectable change in the luminescent properties of the dye.

19(Amended). A method for checking a luminescent substance having particles comprising a dye-laden molecular sieve whose structure forms an optical resonator, comprising the steps:

selecting at least one dye that can be excited to show stimulated emission;

incorporating the dye in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve;

selecting the dye such that the transition to stimulated emission is accompanied by a detectable change in the luminescent properties of the dye; and
using the line narrowing and line shift and/or the threshold behavior and/or the shortening of the lifetime as an authenticity feature.

20(Amended). A process for marking products comprising using dye-laden molecular sieves showing stimulated luminescence without an external resonator for marking the products.

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Document of value

This invention relates to a document of value, such as a paper of value, ID card or the like, having at least one authenticity feature in the form of a luminescent substance. The invention further relates to a security element having at least one authenticity feature in the form of a luminescent substance and to a method for marking products whereby the product is provided with a luminescent substance.

Luminescent substances have been used for some time for marking products in particular for security applications. The advantage of such a marking is that upon suitable illumination of the marked object the luminescent substances emit with high intensity and are thus detectable while areas without the luminescent substances appear substantially dark. In this way the markings can be detected with high sensitivity. Numerous luminescent materials used for marking in the past have very broad emission bands. This is typical in particular of organic dyes, whose luminescence line widths can be several 50 nanometers and more. Many classic inorganic luminescent materials have similar line widths.

EP 0 522 627 A1 describes the production of molecular sieves capable of luminescence and their use as a fluorescent substance for lamps. The reactants (complexing agent and rare earth ions) are incorporated by diffusion in solution into the cavities of zeolites where they react exhaustively into chelate complexes. The chelate complex is fixed in the interior of the cavities.

In addition, colored molecular sieves containing metal salts as the chromophoric component have been known for some time under the name "ultramarine dyes/pigments" (German patent no. 1, 1877). These purely inorganic systems are produced for example by heating zeolite molecular sieves with alkali metal sulfides in a nonoxidizing atmosphere and then in an oxidizing atmosphere at temperatures over 300°C (JP-A-63-017 217; JP-A-55-071 762).

Organic dyes are applied to the molecular sieves normally by treating colorless molecular sieves with dye solutions (see e.g. JP-A-63-017 217; JP-A-53-022 094 and JP-A-75-008 462). In particular in the case of neutral dyes adsorbed only weakly on the molecular sieve framework, there is a danger of the dyes being

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washed off the molecular sieve upon the addition of solvents. An improvement of adhesion is obtained with strongly basic dyes.

It is known to use pigments comprising an inorganic substrate (often laminated minerals, zeolites or zeolite-like materials) and an adsorbed coloring agent in lacquers and water-based paints (JP-PS-75-008 452). When using said pigments it is necessary to select the composition of the paint in such a way that the coloring pigment does not react with the surrounding medium, is insoluble in the solvent used, and deposits uniformly, which is important in particular with mixed colors. This excludes many solvents and binders that are interesting for paint production and greatly restricts the possibilities of mixed color production using the described pigments.

The stated disadvantages are avoided by an irreversible fixation of dyes in the cavities of suitable molecular sieves. DE 41 26 461 describes the production of such materials and their use as pigments and optical data memories. Dyes such as phthalocyanines, phenoxazines, azo dyes, etc., are fixed irreversibly by forming the molecular sieve in-situ around the dye. This technique is generally called "crystallization inclusion" (G. Schulz-Ekloff, "Nonlinear optical effects of dye-loaded molecular sieves," in Advanced Zeolite Science and Application Studies in Surface Sciences Catalysis, Vol. 85 (1994), 145-175). Another method for irreversible fixation of dyes in molecular sieves, "ship-in-the-bottle synthesis," has been described e.g. by G. Meyer et al. (Zeolites 4 (1984), 30). Transition metal-exchanged zeolites are reacted here with o-phthalonitrile, whereby the dye (cobalt, nickel or copper phthalocyanine) is formed in the supercages of approximately 12 angstroms in the faujasite. Since said supercages are only accessible through openings of approximately 7 angstroms to 8 angstroms, the phthalonitrile can diffuse into the cavities but the formed dye cannot diffuse out for steric reasons.

On the basis of said so-called "ship-in-the-bottle" synthesis technique, WO 93/17965, DE 42 07 339 A1 and DE 41 31 447 A1 describe the production of colorants based on molecular sieves. Indigoid dyes, azo dyes and quinizarin dyes are incorporated into molecular sieves from the classes of zeolites and zeolite-like materials.

The described systems and intended uses have in common that the luminescent materials retain their characteristic properties which they also possess in solutions or as powders. By incorporation in the zeolites only slight shifts and broadenings of the spectral bands are observed, in particular with organic dyes. For application as a marking, these effects are not advantageous. Since the emission bands of numerous different luminescent materials overlap, the selectivity of detection of the substances is greatly restricted. Although chemically different materials are present, the differences in their emission bands are often so small that their luminescence must be examined over a broad spectral region with elaborate means to make identification at all possible. For many applications the effort for clear identification is therefore so great that it can be done only in exceptional cases.

The invention is therefore based on the problem of providing a document of value and a security element for marking any products with at least one luminescent material which is easily detected and identified.

This problem is solved by the features of the independent claims. Developments are the subject matter of subclaims.

According to the present invention, the authenticity feature used for documents of value is a luminescent system wherein the line width of dyes is greatly reduced by the effect of stimulated emission in order to permit differentiation of as great a number as possible of characteristic narrow-band luminescence lines of different dye-matrix systems in a selected spectral region. The stimulated emission processes are caused by the dyes being located in a resonator enclosing the dyes. The resonator is formed by a molecular sieve crystallite whose surfaces enclose the luminescence of the dye molecules. The luminescence radiation is coupled out via microdefects in said surfaces.

Said systems are dye-laden molecular sieves which show stimulated emission. They were presented for the first time at the Tenth German Zeolite Conference. These were AlPO-5 type molecular sieves loaded with pyridine-2. The effect was likewise observed on an AlPO-5 molecular sieve that was doped with rhodamine and produced by means of "crystallization inclusion."

According to the invention, however, any other dye-laden molecular sieves which show stimulated emission can also be used. The dyes used may be not only representatives from the classes of pyridines and rhodamines but also dyes from the class of cyanines or coumarins or any other dyes from the class of laser dyes. The spectral properties of the dyes may be adjusted by suitable chemical modification of the chromophore. A plurality of different dyes may also be provided in one molecular sieve.

The molecular sieve used is preferably a molecular sieve with a channel structure and suitable morphology, such as from the classes AFI, LTL, MFI, M41S. Specifically one may use for example AIPO-5, SAPO-5 (AFI class) as well as MAPO and MAPSO, ELAPO and ELAPSO. M stands here for any metal such as Mn, Mg, Co, Fe, Cr, Zn, and EL for an element such as Li, Be, B, Ti, As, Ga, Ge.

In order to increase the light resistance of the material, a UV absorber and/or a UV stabilizer on the basis of sterically hindered amines (HALS) can be embedded, preferably in a dosage of from 0.5 to 3 wt.%, in the cavities of the molecular sieve in addition to the dye. In this way a photostabilization is additionally obtained outside the UV region, in particular at the wavelength of the dye. The UV absorber used can be for example Tinuvin-P, Tinuvin 928 (Ciba Geigy). The sterically hindered amines are for example Tinuvin 144 (Ciba Geigy), Tinuvin 123 (Ciba Geigy), HALS 3051 (Clariant) or derivatives thereof.

Said materials increasing light resistance need not necessarily be incorporated into the cavities of the molecular sieve; they may also be located in or on the internal and external surfaces of the molecular sieve.

If chemical stability is to be increased besides light resistance, antioxidants can also be incorporated into the cavities instead of or in addition to the UV stabilizers or UV absorber.

The invention is based on the finding that said systems are very advantageously suited for marking applications since an intraparticle resonator is used for greatly reducing the luminescence line width of the system upon suitable excitation. This permits differentiation of a large number of different dyes via the spectral positions of their luminescence spectra. That is, said dyes can be used to represent a plu-

ality of codings. The number of different markings can be increased even further by additionally evaluating the intensity of the emitted radiation, which is proportional to the quantity of luminescent material or dye present.

The inventive idea can thus be used to form a great variety of coding systems. For example, an object can be marked with different ones of the above-described dyes. The coding then arises through the presence or absence of one or more particles.

However, coding systems are also possible involving variation of both number and structure (selection of dye-molecular sieve combination). Weak excitation thus gives rise to an opaque mixed spectrum that is difficult to separate spectrally. Only strong excitation causes the above-described particles to reveal their special property and stand out from the broad-band luminescence spectrum of the mixture.

The characteristic properties of the dye-molecular sieve systems show themselves only upon intensive optical excitation with light of a suitable wavelength. Due to the threshold behavior of the systems, the optical irradiance must exceed a threshold value characteristic of the systems. Typical threshold values are 0.2 to 4 megawatts per square centimeter. The excitation source may be a light source of suitable wavelength with sufficient radiation capacity. An optical apparatus can be used to focus the light of the excitation source on a sufficiently small spot and thus increase the irradiance of the systems.

In the following some examples of the dyes or authenticity features to be used according to the invention will be stated.

Example 1

Dyes from the class of pyridines are enclosed in a suitable molecular sieve such as a SAPO-5 molecular sieve. Upon excitation with a frequency-doubled Nd:YAG laser the dye-laden molecular sieve absorbs in the region of the laser wavelength of 532 nanometers. At a laser power density of 4 megawatts per square centimeter the dye-laden molecular sieve shows a very narrow-band laser-like fluorescence spectrum in the region of approximately 680 nanometers.

Example 2

A dye from the class of rhodamines is enclosed in a suitable molecular sieve belonging e.g. to the structure type MFI, LTL, EMT, M41S, AFI, CHA. Upon excitation with a frequency-doubled Nd:YAG laser and at a laser power density of 4 megawatts per square centimeter this material shows a very narrow-band laser-like fluorescence spectrum in the region of 560 nanometers.

Example 3

A dye from the class of coumarins is enclosed in a suitable molecular sieve such as an AlPO-5 molecular sieve. Upon excitation with an XeCl excimer laser with a wavelength of 308 nanometers and a laser power density of 4 megawatts per square centimeter the molecular sieve shows a very narrow-band laser-like fluorescence spectrum in the region of 530 nanometers.

Detection of the systems must involve the detection of at least one of the following characteristic properties of the systems to permit a delimitation over conventional luminescent materials without stimulated emission.

The characteristic increase in intensity in a narrow wave range upon supraliminal excitation can be detected upon observation through the characteristic threshold behavior of the increase in intensity when irradiance is increased by means of a suitable spectrally narrowing element in the detection channel.

Characteristic luminescence line narrowing can be detected by comparison of the intensities in the narrow wave range characteristic of the dye system with the intensity in other wave ranges. This is done e.g. by means of a spectrometer setup with sufficient spectral resolution or by measurement in different detection channels which measure the intensity in the required spectral region through suitable spectrally selective elements. Upon supraliminal excitation a characteristic spectral distribution is observed with an intensity peak at the characteristic wavelength or characteristic intensity relations in the different channels which do not occur with conventional luminescent dyes.

The characteristic shortening of the lifetime of luminescence at the characteristic wavelength of the dye system to typically under 300 picoseconds likewise permits differentiation of the systems from conventional luminescent dyes (typical lifetime over 3 nanoseconds). This requires excitation sources whose turn-off times are clearly shorter than the lifetime of conventional luminescent dyes. The decay times of detector and detection electronics must also be comparably fast.

As a further characteristic property of the systems, the saturation of the optical transition occurs only at very much higher luminescence intensities, so that much higher luminescence intensities can be observed with these systems than with conventional luminescent materials.

Upon suitable synthesis the described molecular sieves form microcrystals or crystal-like structures, to be referred to as particles in the following. The particles can be used directly for marking any objects, in particular papers of value, passports, forms, CDs or other products of daily use. The simplest possibility is to add the particles to a printing ink. The particles can also be added directly to the material of the object, however. This is expedient for example if the object to be protected is a document of value such as a bank note or ID card. In the case of the bank note, the particles are preferably added to the paper pulp during production of the bank note paper. With ID cards, however, one of the cover or inlay layers can be mixed with the particles in its volume. The particles can likewise be embedded directly in a polymer.

According to another embodiment, the inventive authenticity feature or dye-laden molecular sieves can also be combined with a kind of camouflage material. In this case two luminescent materials are used for producing a marking, one of the materials being a conventional luminescent material and the other an inventive dye-laden molecular sieve. Upon subliminal excitation both materials behave the same way, while upon supraliminal excitation the emission behavior of the dye-laden molecular sieve changes, as explained above. If for example a bar code is printed with the inventive particles and the spaces in the bar code with conventional luminescent material, subliminal excitation permits detection of only a uniformly luminescent field. Supraliminal excitation of the inventive particles results in narrow lumines-

cence peaks in the emission spectrum in the area of the bars of the code, thereby making the code visible. This principle can of course also be used to represent any other codings or information.

The materials, conventional luminescent material and inventive molecular sieve, may also be contained jointly in a printing ink or another carrier material. In this case, supraliminal excitation of the molecular sieve serves as an additional authenticity feature and thus increases forgery-proofness.

Further examples and advantages of the invention will be explained with reference to the figures. It is pointed out that these are merely schematic diagrams which raise no claim to completeness or true-to-scale representation.

Fig. 1 shows an inventive document of value with an inventive authenticity feature,

Fig. 2 shows a section along A - A of the document of value in Fig. 1,

Fig. 3 shows a section along A - A of another embodiment of the inventive document of value,

Fig. 4 shows an absorption spectrum of an inventive authenticity feature,

Fig. 5 shows an emission spectrum of an inventive authenticity feature,

Fig. 6 shows the behavior of the emission intensity as a function of the excitation intensity of an inventive authenticity feature.

Fig. 1 shows inventive document of value 1 with inventive security element 2. In the shown example, security element 2 consists of an area shown by the dash line in which the actual authenticity feature, print 3, is disposed. Print 3 contains the inventive dye-laden molecular sieve particles.

Alternatively, security element 2 could also be designed in the form of a label bearing authenticity feature 3 in the form of a print. It is likewise possible to design security element 2 in the form of a thread or band, authenticity feature 3 being disposed on a carrier material, preferably a plastic foil. Said band can be either disposed all over the surface of document of value 1 or embedded at least partially into the document of value. This manner of incorporation is expedient in particular with bank notes, which are frequently provided with so-called "window security threads."

The security thread is woven here quasi into the paper during its production so that it passes directly to the surface of the paper in certain areas.

Fig. 2 shows the document of value shown in Fig. 1 along line A - A in cross section. Print 3 on document of value 1, which forms the authenticity feature in the present case, contains particles which are formed by a dye-laden molecular sieve. Authenticity feature 3 is usually invisible in normal illumination, becoming recognizable only after excitation with corresponding radiation. Depending on the desired effect, authenticity feature 3 or the print forming authenticity feature 3 can also contain further dyes that are actually visible visually. It must be ensured, however, that said additional dyes have no appreciable absorption in the emission wave range of the inventive particles.

Fig. 3 shows another embodiment of inventive document of value 1 in cross section along line A - A. Here security feature 2 does not consist only of authenticity feature 3 in the form of a print but additionally has camouflage print 4 surrounding authenticity feature 3 in the total area of security element 2. That is, the area shown by the dash line in Fig. 1 is provided completely with camouflage print 4 except for the area of authenticity feature 3. Camouflage print 4 contains a usual luminescent material, which is likewise transparent preferably in the visible spectral region. Additionally, said luminescent material shows the same absorption and emission behavior as the inventive particles as long as it is excited with a laser power density below the threshold value characteristic of said particles. In this way a corresponding detector can perceive security element 2 only as a uniformly luminescent surface upon subliminal excitation. Upon supraliminal excitation the emission behavior of authenticity feature 3 changes and the marking shown by authenticity feature 3 stands out in the form of narrow, very high-intensity emission lines from the luminescent background formed by camouflage print 4.

Fig. 4 shows the absorption spectrum of an inventive dye-laden molecular sieve in the region of 530 nanometers.

If a light source with low radiation density is used for irradiating authenticity feature 3, the authenticity feature shows relatively broad-band luminescence emission which is based on spontaneous emission and shown in Figure 5 by curve A.

Fig. 6 illustrates this state of affairs. Emission intensity of I_E grows only slowly with the excitation intensity below threshold I_S . Above threshold value I_S the stimulated emission of the dye-laden molecular sieve sets in so that the emission intensity grows very much faster with the excitation intensity. Here, the molecular sieve surrounding the dye acts like a laser resonator which intensifies the luminescent radiation emitted by the dye like a laser.

According to the invention a plurality of particles consisting of different dye-laden molecular sieves can also be mixed together. Subliminal excitation thus gives rise to a practically unresolvable emission spectrum since the relatively broad emission bands of the individual luminescent dyes greatly overlap. Only supraliminal excitation causes the emission lines of the individual dyes to narrow very greatly and show the above-described laser-like behavior. In this state the individual spectral lines of the dyes can be distinguished very well from each other.

Claims

1. A document of value (1), such as a paper of value, ID card or the like, having at least one authenticity feature (3) in the form of a luminescent substance, the luminescent substance (3) having particles consisting of a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission, the dye being incorporated in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve and the transition to stimulated emission being accompanied by a detectable change in the luminescent properties of the dye.

2. A document of value (1) according to claim 1, characterized in that the luminescent substance (3) has different particles consisting of different dye-laden molecular sieves.

3. A document of value (1) according to claim 1 or 2, characterized in that molecular sieves with a channel structure, e.g. from the classes of aluminophosphates, are used.

4. A document of value (1) according to at least one of claims 1 to 3, characterized in that the dye molecules from the class of laser dyes are used.

5. A document of value (1) according to at least one of claims 1 to 4, characterized in that the spectral properties of the dye are adjusted by selection of the end groups.

6. A document of value (1) according to at least one of claims 1 to 5, characterized in that the molecular sieve has different excitable dyes.

7. A document of value (1) according to at least one of claims 1 to 6, characterized in that the document of value (1) has a further authenticity feature.

8. A document of value (1) according to claim 7, characterized in that the second authenticity feature is a further luminescent material which preferably has the same body color as the luminescent substance.

9. A document of value (1) according to at least one of claims 1 to 8, characterized in that the luminescent substance (3) is present in the volume of the document of value (1).

18. A method for marking products whereby the product is provided with a luminescent substance having particles consisting of a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission, the dye being incorporated in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular

sieve, and the transition to stimulated emission being accompanied by a detectable change in the luminescent properties of the dye.

19. A method for checking a luminescent substance having particles consisting of a dye-laden molecular sieve whose structure forms an optical resonator in which at least one dye can be excited to show stimulated emission, the dye being incorporated in the cavities of the molecular sieve or located in or on the internal and external surfaces of the molecular sieve, and the transition to stimulated emission being accompanied by a detectable change in the luminescent properties of the dye, the line narrowing and line shift and/or the threshold behavior and/or the shortening of the lifetime being used as an authenticity feature.

20. Use of dye-laden molecular sieves showing stimulated luminescence without an external resonator for marking products.

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FIG.1

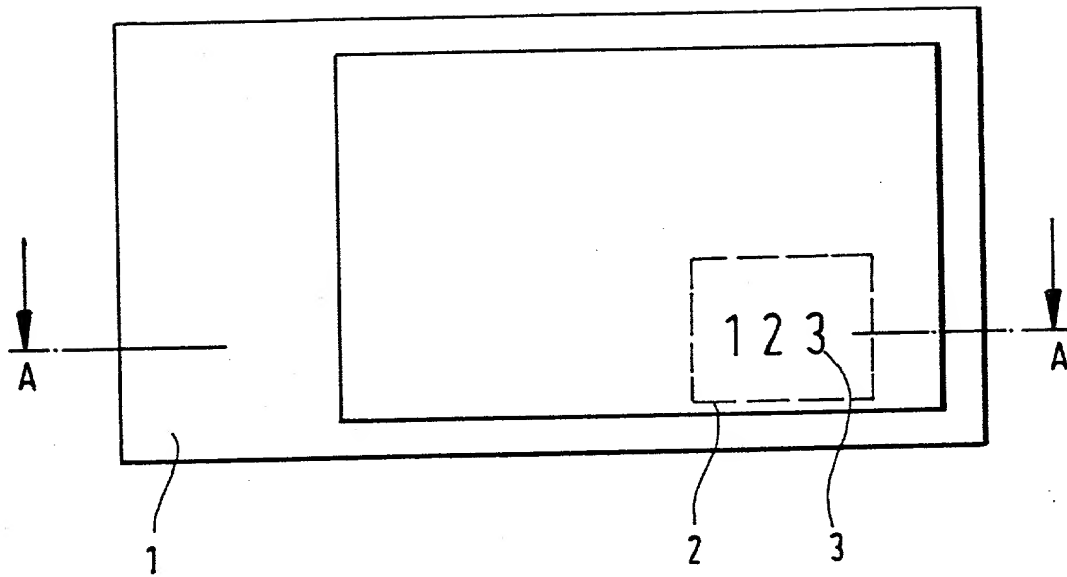
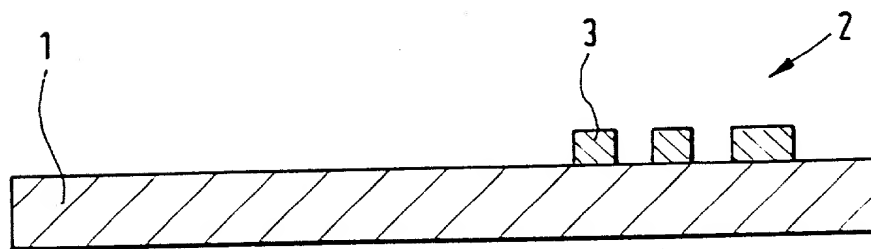


FIG.2



2/3

FIG. 3

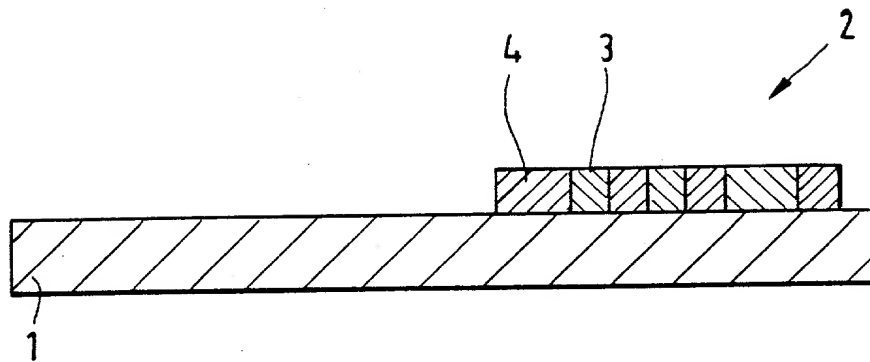
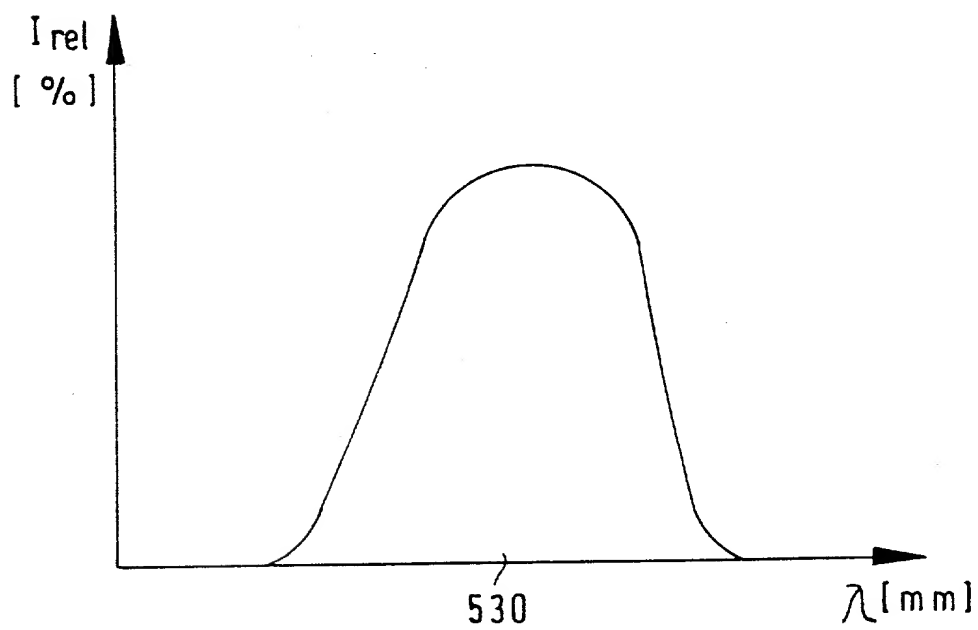


FIG. 4



3/3

FIG.5

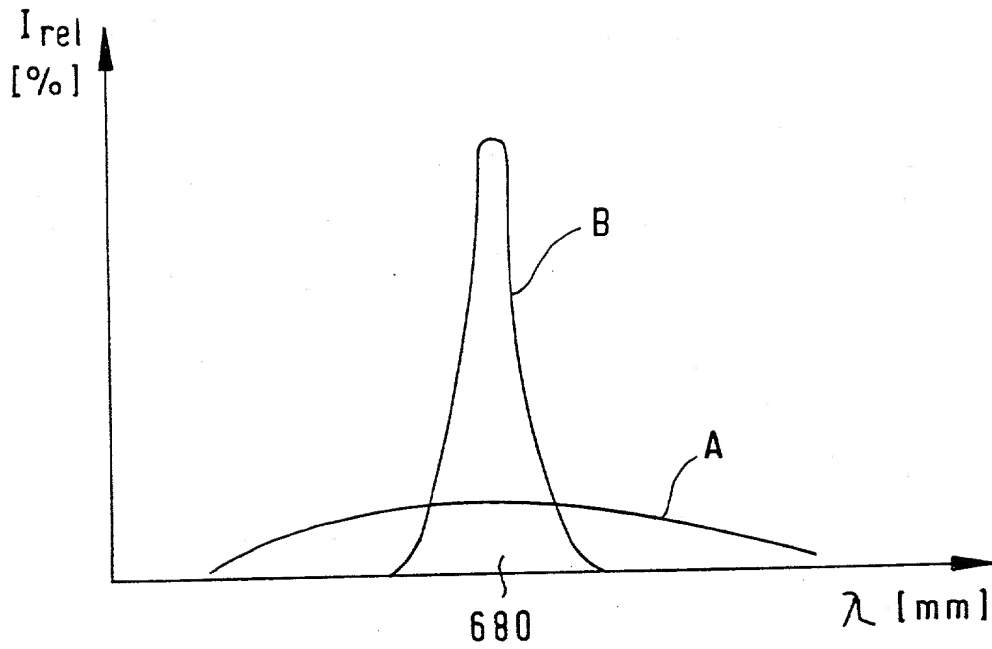
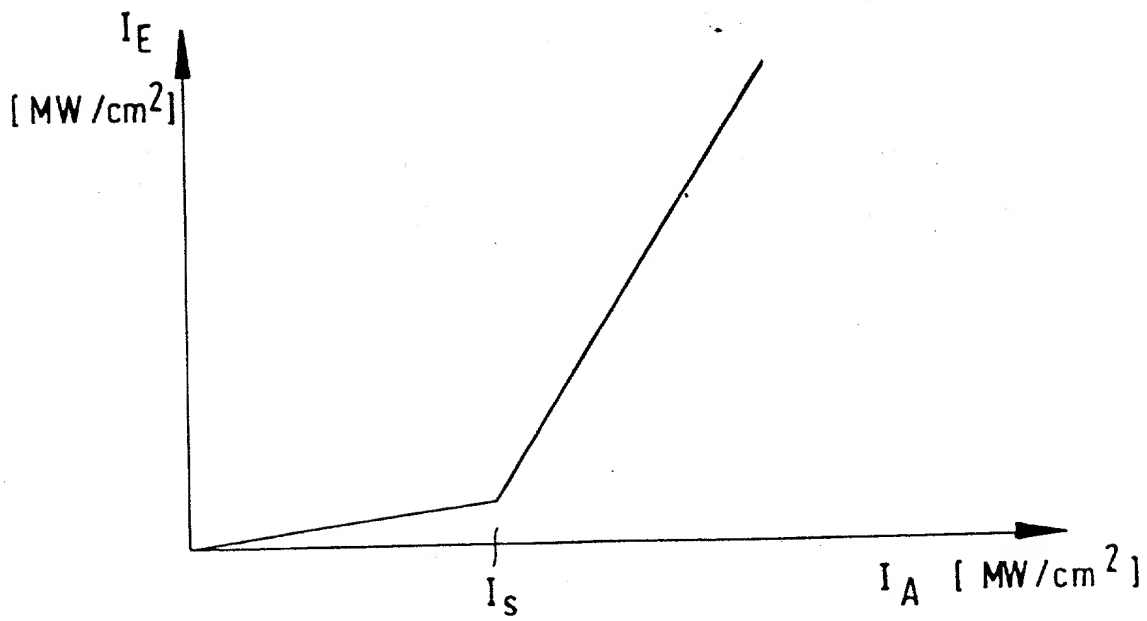


FIG.6



DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention (Design, if applicable) entitled:

VALUABLE DOCUMENT

the specification of which (check one):

☐ is attached hereto, or ☒ was filed on: **23 May 2000**

Application Number: **(PCT/EP00/04694) 09/926,579**

as U.S. Application Number or PCT International
and (if applicable) was amended on:

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in *Title 37, Code of Federal Regulations, §1.56*. I hereby claim foreign priority benefits under *Title 35, United States Code §119* of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)			PRIORITY CLAIMED	
Number	Country	Day/Month/Year Filed	Yes	No
199 23 959.2	Germany	25 May 1999	X	

☐ Additional Priority Application(s) Listed on Following Page(s)

I HEREBY CLAIM THE BENEFIT UNDER TITLE 35 U.S. CODE §119(E) OF ANY U.S. PROVISIONAL APPLICATIONS LISTED BELOW.

Application Number	Day/Month/Year Filed

☐ Additional Provisional Application(s) Listed on Following Page(s)

I hereby claim the benefit under *Title 35, United States Code, §120* of any United States application(s) or PCT international application(s) designating The United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of *Title 35, United States Code, §112*, I acknowledge the duty to disclose information which is material to patentability as defined in *Title 37, Code of Federal Regulations, §1.56* which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Application Number	Filing Date	Status - Patented, Pending or Abandoned

☐ Additional US/PCT Priority Application(s) listed on Following Page(s)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under *section 1001 of title 18 of the United States Code* and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: I (We) hereby appoint as my (our) attorneys, with full powers of substitution and revocation, to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: J. Ernest Kenney, Reg. No. 19,179; Eugene Mar, Reg. No. 25,893; Richard E. Fichter, Reg. No. 26,382; Thomas J. Moore, Reg. No. 28,974; Joseph DeBenedictis, Reg. No. 28,502; Benjamin E. Urcia, Reg. No. 33,805; and

I(we) authorize my(our) attorneys to accept and follow instructions from Klunker Schmitt-Nilson Hirsch regarding any matter related to the preparation, examination, grant and maintenance of this application, any continuation, continuation-in-part or divisional based thereon, and any patent resulting therefrom, until I(we) or my(our) assigns withdraw this authorization in writing.

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☒ See following page(s) for additional joint inventors.

CONTINUATION OF DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

Page 2

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Number	Country	Day/Month/Year Filed	Yes	No

PRIOR PROVISIONAL APPLICATIONS 35 U.S. CODE §119(E)	
Application Number	Day/Month/Year Filed

PRIOR U.S. OR PCT INTERNATIONAL APPLICATIONS (35 U.S. CODE §120)		
Application Number	Filing Date	Status - Patented, Pending or Abandoned

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DATE <i>12/22/2001</i>	SIGNATURE <i>Thomas Attenberger</i>	

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DATE	SIGNATURE	

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DATE	SIGNATURE	

☐ See following pages for additional joint inventors/priority applications.

DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention (Design, if applicable) entitled: **VALUABLE DOCUMENT** the specification of which (check one):

☐ is attached hereto, or ☒ was filed on: **23 May 2000**

as U.S. Application Number or PCT International

Application Number: **PCT/EP00/04694**

and (if applicable) was amended on:

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in *Title 37, Code of Federal Regulations, §1.56*. I hereby claim foreign priority benefits under *Title 35, United States Code §119* of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

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I(we) authorize my(our) attorneys to accept and follow instructions from klunker Schmitt-Nilson Hirsch regarding any matter related to the preparation, examination, grant and maintenance of this application, any continuation, continuation-in-part or divisional based thereon, and any patent resulting therefrom, until I(we) or my(our) assigns withdraw this authorization in writing.

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DATE <u>23 May 2000</u>	SIGNATURE

☒ See following page(s) for additional joint inventors.

CONTINUATION OF DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

Page 2

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